THE FLUOROCARBON RELEASE PROBLEM

A Review for the Hawaii State Legislature
Responsive to H.R. 528, HD 1 (1976)

by

Wan-Cheng Chiu, Department of Meteorology
Michael J. Chun, Department of Public Health
Doak C. Cox, Environmental Center
Peter M. Kroopnick, Department of Oceanography
Thomas A. Schroeder, Department of Meteorology
Sanford M. Siegel, Department of Botany

Environmental Center
University of Hawaii

February 1977

THE FLUOROCARBON RELEASE PROBLEM

A Review for the Hawaii State Legislature
Responsive to H.R. 528, HD 1 (1976)

Contents

Summary 1
Scope and preparation of report 2
Chemical terminology 2
Sources and rates of release of fluorocarbons and other halomethanes 3
Fate of halomethanes 4
Dispersion of halomethanes 4
Effects of halomethane release on ozone 5
Indirect effects on ultraviolet radiation 5
Indirect effects on halomethane releases on health 6
Benefits and costs of chlorofluoromethane release controls . . 7
Recent pertinent recommendations 7
Effectiveness of state legislation 8
References 9

Summary

H.R. 528, HD 1 requested that the Environmental Center report annually on the findings of research related to the effects of fluorocarbon release to the atmosphere on ozone concentrations, and recommend on pertinent legislation. This report summarizes present information relating not only to the specific effects cited, but to the sources of the fluorocarbons and to the health effects of the increases in ultraviolet light penetration that results from ozone depletion in the stratosphere.

The problem of the health effects resulting indirectly from fluorocarbon releases is seen to be worldwide and Hawaii's contribution to the problem, either in general or in Hawaii specifically, is minor. The problem is now well recognized at national and international levels. However, the magnitude of the problem may be much smaller than has hitherto been recognized generally because, it appears, the natural release has generally been overlooked in estimating the consequences of fluorocarbon releases.

No Hawaii legislation related to fluorocarbon uses is recommended under present circumstances, other than a resolution cancelling the request that the Environmental Center continue formal annual reporting annually on the problem.

THE FLUOROCARBON RELEASE PROBLEM

A Review for the Hawaii State Legislature
Responsive to H. R. 528, HD 1 (1976)

Scope and preparation of report

H.R. 528, HD 1 (Appendix B) requested that the Environmental Center report annually on new research findings pertinent to the theory that fluorocarbon releases result in depletion of the ozone in the atmosphere and make recommendations on appropriate State legislative action.

The appropriateness of legislative action has been seen by the Center as dependent, not only on the nature and effectiveness of the fluorocarbon-ozone reaction, but on the sources and benefits from the use of fluorocarbon compounds; on the effects of decreases in ozone concentration, resulting from atmospheric releases of fluorocarbons, on ultraviolet light penetration; on the effects of resulting increases in ultraviolet light penetration on human health; on cost/benefit comparisons weighing the human health detriments against the benefits of fluorocarbon usage and costs of control; and on the evaluation of Hawaii's share in contributing to and suffering from the problem.

To review both the specific recent research findings identified in the resolution and the status of the problem more generally, a Center task force was appointed, as represented by the authorship of this report.

Chemical terminology

The resolution mentioned fluorocarbons alone, that is components of fluorine and carbon. There is a component of fluorine and carbon alone, carbontetrafluoride (or tetrafluoromethane) (CF_4). However, the components of concern, the Freons, CCl_2F_2 and $CFCl_3$, include chlorine as well. These are members of the general group of halomethanes, compounds of carbon and one or more of the halogens: iodine (I), bromine (Br), chlorine (Cl), and Fluorine (F); with or without hydrogen (H). The chemical bonds are such that, in one of these compounds, for each carbon atom there must be a total of four atoms of halogen or hydrogen. The artificial manufacture of Freons and related components start from carbontetrachloride (or tetrachloromethane) (CCl_4).

In the discussion following, reference will be made to the halomethanes as a group, to the fluorocarbons, or to individual compounds by chemical formula, as pertinent.

Sources and rates of release of fluorocarbons and other halomethanes

Artificial Sources

It has generally been assumed that the significant sources of fluorocarbons in the atmosphere are releases of these substances manufactured by human use.

The world production of artificial sources of fluorocarbons is about 1000 or 2000 million pounds per year (Peterson and Stuiver, 1975; McCarthy, 1974). The U.S. production is about half of the total.

The production of Freons, and other increases in the use of halomethanes have resulted in great increases in the rate of production of carbontetrachloride, the rate of production in the U.S. having increased several hundred times between 1913 and 1974 (Altschuler, 1976).

About half of the fluorocarbons produced goes into the manufacture of aerosols, whose use involves their essentially total release to the atmosphere.

The major use of the remainder is in refrigeration. The refrigerants are released to the atmosphere through leakage and upon discard of refrigeration equipment.

It then appears that the artificial release of fluorocarbons to the atmosphere is on the order of 1000 million pounds or 0.5 megatons per year.

Natural Sources

In estimating the effects of fluorocarbon releases to the atmosphere, the possible significance of natural sources of halomethanes seems generally to have been overlooked.

Lovelock (1975) determined that the concentration of CHI_3 and other halomethanes over kelp beds is more than a thousand times the concentration over open-ocean sites, and suggested that CH_3Cl , in or near southern England was from non-human sources. Earlier, Lovelock *et al.* (1973) had estimated annual release rates from the open sea halomethanes, in megatons, to be 0.44 for CCL_3F, 40 for CH_3I, and 1.7 for CCl_4. They also pointed out that CCl_4 concentrations in southern tropical regions, where the release from human sources was much smaller, were similar to those of the northern hemisphere. Conkle *et al.* (1975) have identified several halomethanes in human respiratory gas which cannot be accounted for from external sources. Stoiber (1971) has demonstrated that volcanoes are sources of halocarbons.

Siegel *et al.* (in preparation) have argued from theoretical biochemical consideration for a possible release of biogenic CH_3Cl of 30 megatons annually.

Summary

It would thus appear that the rates of halomethane release from natural sources to the atmosphere may be far greater than rates of release from artificial sources.

Fate of halomethanes

Halomethanes are released at the earth's surface. Subsequent dispersal involves transport into the troposphere and eventually into the stratosphere. We consider here the processes that occur prior to and during the transport to the stratosphere (Rowland and Molina, 1975).

Immediately after release the low density halomethanes begin to rise into the atmosphere. Many pollutants are subsequently returned to the soil via rainfall. However, the extremely low solubility of most halomethanes precludes their removal in this manner. This relative insolubility in water together with their high chemical stability (especially toward hydrolysis) indicates that these compounds will not be rapidly removed by dissolution in groundwater or the oceans. Mixing into the deep sea is a process requiring hundreds of years and a stable equilibrium will have to exist between the troposphere and the stratosphere for a long time before any substantial amount of halomethanes will penetrate below the oceanic thermocline.

Details about possible biological interactions of these compounds are very scarce. Since the fluorochloromethanes are almost entirely of recent anthropogenic origin and are chemically very inert, the halomethanes are expected to be almost totally unreactive, biologically speaking. Experiments indicate that soils and plants do not act as sinks for either CF_2Cl_2 or $CFCl_3$. Thus biological removal of halomethanes from the troposphere seems highly unlikely.

Photochemical decomposition of those halomethanes containing hydrogen atoms may begin in the troposphere but the bulk of the decomposition of these compounds as well as the non-hydrogen containing ones occurs in the stratosphere. The photochemical reactions involved in this decomposition are discussed in detail elsewhere. Thus, except for CHF_2Cl and CH_3Cl, no tropospheric sink has been found for the halomethane, and hence vertical transport into the stratosphere appears to be the major removal process from the troposphere.

Dispersion of halomethanes

The major mechanisms that are responsible for the dispersion of particles, whether they be dust, or gases, such as freon, are atmospheric turbulence, weather-producing systems, and meridional circulation.

In the surface boundary layer (a thin layer immediately above the ground, say of the order of tens of meters), the mixing and dispersion of particles are carried out mostly by small-scale turbulences. Above that layer the dispersion and mixing of particles are carried out by small-scale turbulence as well as larger-scale moving systems, such as cumulus convections, thunderstorms, hurricanes, midlatitude cyclones and anticyclones, etc. Through the vertical motions associated with these systems, particles may be carried to the upper troposphere. From there, they are further carried into the stratosphere through the broken tropopause above the jet stream by the quasi-horizontal mixing motion, or through the tropical tropopause by the strong cumulus convections in the ascending branch of the meridional circulation that sometimes penetrates into the stratosphere. (A meridional circulation is a circulation in the tropics that consists, on the average, in an ascending motion in the subtropics, and a returning southward motion in the lower troposphere. The northeast trades that prevail in the Hawaiian Islands are part of this circulation.)

It is difficult to say how long it takes for some of the particles that originate at ground level to reach the stratosphere, for the mechanisms that affect the transfer are many, their strengths vary with space and time, and what happens to a particle depends on the chain of events that it encounters. A violent thunderstorm can pick up particles from the ground and transport them into the stratosphere within hours. On the other hand, in relatively placid air, particles may tend to settle back to the ground rather than go further up the sky. It is likely that particles may be carried up sometimes and down other times. Whether they end up on the ground or in the stratosphere depends on the history of motions that they have encountered. But this is not important to the problem at hand. What is important is that as long as there are halomethanes released on the ground level, some of them will eventually end up in the stratosphere, and the more they are released, the more there are likely to be in the stratosphere later.

Effects of halomethane release on ozone

Stratospheric ozone is created by a two-stage process. Molecular oxygen dissociates upon absorption of ultraviolet radiation of wavelengths less than 0.26 micrometers. The monatomic oxygen produced reacts with additional molecular oxygen in the presence of a catalytic agent (typically molecular nitrogen) to produce triatomic oxygen or ozone. Ozone production is balanced by photodissociation. Ozone absorbs ultraviolet radiation in wavelengths up to 0.32 micrometers, creating monatomic oxygen and molecular oxygen. The influence of absorption by ozone is an increase of temperature with height in the stratosphere.

The fluorocarbons and other halomethanes also absorb ultraviolet radiation upon reaching the stratosphere. This process liberates free chlorine atoms which enter into reactions with stratospheric ozone providing an additional ozone sink. Uncertainties in the reaction rates for important stratospheric chemical reactions causes estimates of ozone depletion to vary. Current estimates based on fluorocarbon production continued at 1973 rates range from 2 to 20 percent with 7 percent as the most commonly agreed upon figure. As previously noted, however, these estimates do not take into account the effects of natural releases of halomethanes. Considerable support exists in the scientific community for two more years of intensive research prior to final action on fluorocarbon production. (Estimates of the effects of two additional years of fluorocarbon production are less than 0.5 percent ozone depletion.)

Indirect effects on ultraviolet radiation

Ozone is the principal atmospheric screen to ultraviolet radiation in the band between 0.26 and 0.32 micrometers. A depletion of stratospheric ozone concentrations must be reflected in a corresponding increase in ultraviolet penetration to the earth's surface. Consequences of increased ultraviolet penetration are discussed in the following section.

Indirect effects of halomethane releases on health

Biological life is dependent on the screening of ultraviolet (UV) radiation in the stratosphere, primarily accomplished by the ozone layer. It appears that reduction of the ozone layer due to the use of fluorocarbons will result in an increase in the intensity of UV radiation transmitted to the earth's surface. Biological damage caused by UV radiation from 295 to 320 nm coincides with the band whose intensity at the earth's surface is most affected by alterations in stratospheric ozone concentrations (Climatic Impact Committee, 1975, p. 36).

The major health effects of biologically active UV rays (DUV) that may occur as a consequence of a reduction in the ozone layer are related to skin cancer (Committee on Impacts of Stratospheric Change, 1976). Cancer in humans caused by excessive exposure to the sun is well documented. Generally, studies have shown that Caucasians are significantly more sensitive to increased exposure to the sun than heavily pigmented persons. Therefore, fair skinned populations are particularly more susceptible to the effects of increased UV radiation (Climatic Impact Committee, 1975, p. 179). It is known that wavelengths effective in producing erythema (sunburn) are below 320 nm. Skin injury caused by the sun is most likely the principal stress factor in inducing skin cancer, especially since sunburn and skin cancer arise in the same tissue (Climatic Impact Committee, 1975, p. 179). There is also supporting evidence that skin cancer is the result of changes in DNA which may be related to the mutagenic effects of UV light. The effect of UV radiation on human skin is a cumulative process; malignancies may be induced with repeated exposure to DUV (Ahmed, 1975).

Malignant skin tumors fall into two categories: malignant melanoma and non-melanoma carcinoma. Malignant melanoma is considered to be the most dangerous form of skin cancer. It is less prevalent than non-melanoma carcinoma but highly fatal since it readily produces secondary tumors which metastasize to other parts of the body. Forty percent of patients with this form of cancer die within five years after the outset of the disease.

Non-melanoma skin cancer includes squamous cell and basal cell carcinoma. Squamous cell carcinoma is prevalent among Caucasian populations exposed to excessive sunlight. Exposed parts of the body and the upper extremities are most affected but with early treatment this form of skin cancer is generally non fatal (Ahmed, 1975, citing Smith, 1973). Basal cell carcinoma occurs in facial tissues and, if untreated, causes severe disfiguration. Medical treatment is usually effective since these tumors are generally localized and do not metastasize readily.

It is generally accepted that for a 10 percent loss of atmospheric ozone, there will be at least a 20 percent increase in the incidence of skin cancer (Climatic Impact Committee, 1975). A 10 percent loss of ozone would cause 60,000 to 200,000 additional diagnosed cases of skin cancer per year in the United States (Ahmed, 1975, p. 12). Similarly, on a worldwide basis, a 10 percent ozone loss will result in 300,000 to 1,000,000 additional detected cases of skin cancer yearly in Caucasian populations (Ahmed, 1975).

Long term exposure to lower wavelength UV radiation is also believed to lead to a number of chronic skin changes, such as wrinkling, thinning and discoloration of the skin (Ahmed, 1975). Sufficient quantitative data, however, are lacking, so it has not been possible to quantify a relationship between prematurely-aged skin and solar radiation.

Benefits and costs of chlorofluoromethane release controls

The uses of Freons in aerosols and refrigerants have been noted previously. No controls of the release of Freon aerosols would be possible except through controls of the distribution and use of these aerosols. Some control of the releases of the Freon refrigerants might be achieved through redesign of the equipment in which they are used, to reduce the likelihood of leakage, and through regulation of the means used to repair and dispose of such equipment.

We have not attempted to estimate either the economic costs of such controls or to estimate the benefits.

Most of the costs of eliminating the use of Freon aerosols would be simply inconvenience. Mechanical spraying or direct application could be used in place of aerosol dispersal in most cases. The costs of either substituting other refrigerants for the Freons or of reducing the likelihood of their releases to the atmosphere would, however, be considerable.

The benefits of the controls in terms of human health might possibly be considerable, but the evidence is tenuous. In the light of the natural rates of production and release of halomethanes, it seems quite doubtful that the benefits would outweigh the costs, except perhaps in the case of the aerosols.

Recent pertinent recommendations

The National Research Council's Committee on Impacts of Stratospheric Change recommended in October 1976 that, unless new findings emerge to mitigate the threat, nonessential uses of the halomethanes should be drastically curtailed. The Council's Panel on Atmospheric Chemistry after a thorough review of the state of knowledge about ozone also issued a report in October 1976.

Based on these two committee reports the Council recommended that chlorofluoromethanes not be used in aerosol cans after January 1978. More important uses of chlorofluoromethane, such as in refrigeration, would be phased out more slowly, but only if curtailment of other sources did not provide sufficient control and only if reasonable alternatives became available. The recommendations are summarized in Appendix A.

Two pertinent reports recently published by the National Academy of Sciences (1976a, 1976b) may have additional information and detail supporting these recommendations, but these are not yet available to us.

Effectiveness of State legislation

The significant problem with the release of fluorocarbons and other halomethanes to the atmosphere is the detriment to human health resulting indirectly by way of the halomethane reaction with ozone and the effects of ozone depletion on ultraviolet light penetration. The magnitude of the problem is not clear, especially because natural releases of halomethane have not been taken into account. It is clear, however, that the major contributions to this problem are distributed among the developed nations of the world. The United States is a major contributor, but Hawaii's part of that contribution is only a very small one. It is also clear that the human health detriments are worldwide, that the detriments in Hawaii are no greater than elsewhere, and the detriments in Hawaii have no relation to the local contribution to the problem. Hence, it is clear that controls of fluorocarbon uses or releases in Hawaii will have no significant effect in reducing the detriments.

State legislation calling for the regulation of fluorocarbon uses or releases in Hawaii would, therefore, be of no significant value. The only State legislation that would conceivably be of significant value would be resolutions calling for national or international regulation of fluorocarbon uses or releases. The problem is now well recognized at national and international levels and, at these levels, concerns in Hawaii would properly be regarded as of no special importance.

The fluorocarbon problem will continue to be a concern of the Environmental Center, and the Center will bring to the attention of the Legislature any developments that seem to be of special Hawaiian interest. However, the continuance of a specific responsibility for periodic report to the Legislature does not seem warranted. Hence, we recommend against the passage of any legislation pertaining specifically to the fluorocarbon problem by the Hawaiian Legislature under the present circumstances, other than a resolution cancelling the request that the Environmental Center continue to report annually on the problem.

References

Ahmed, A.K. 1975. "Unshiedling the Sun: Human Effects," Environment, 17: 6-14. April 1975.

Alfschuler, A.P. 1976. "Average Tropospheric Concentration of Carbontetrachloride Based on Idustril Production, Usage, and Emissions," Environ. Sci. & Tech. 10: 596-598.

Climatic Impact Committee. 1975. "Biological and Medical Effects of NO_x Emissions," Environmental Impact of Stratospheric Flight. National Academy of Sciences.

Committee on Impacts of Stratospheric Change. 1976. "Halocarbons and Ozone." News release, National Research Council. November 1976.

Conkle, J.P.; B.J. Camp; and B.E. Welch. 1975. "Trace Composition of Human Respiratory Gas," Arch. Environ. Health 30: 290-295.

Lovelock, J.E.; R.J. Maggs; and R.J. Wade. 1973. "Halogenated Hydrocarbons in and Over the Atlantic," Nature 241: 194-196.

Lovelock, J.E. 1975. "Natural Halocarbons in the Air and in the Sea," Nature 256: 193-194.

McCarthy, R. 1974. "Fluorocarbons in the environment." Abstract, Amer. Geophys. Union Ann. Mtg., San Francisco.

National Academy of Sciences. 1976a. "Halocarbons: Effects on Stratospheric Zone."

National Academy of Sciences. 1976b. "Halocarbons: Environmental Effects of Chlorofluoromethane Release.

Peterson, R.; S. Peterson; and H. Guyford. 1975. "Fluorocarbons and the Environment." Official release, Interagency Task Force on Inadvertent Modification of the Stratosphere (IMOS), 12 June 1975.

Rowland, F.S. and M.J. Molina. 1975. "Chlorofluoromethanes in the Environment," Reviews of Geophysics and Space Physics 13: 1-35.

Smith, K.C. 1973. "Biological Impacts of Increased Intensities of Solor Ultra Violet Radation." Report to the Environmental Studies Board. (Washington, D.C.: National Academy of Sciences, 1973.)

Stoiber, R.E.; D.C. Leggett; T.F. Jenkins; R.P. Murrmann; and W.I. Rose, Jr. 1971. "Organic Compounds in Volcano Gas from Santi Aquito Volcano, Guatomala." Geol. Soc. Amer. Bulletin 82: 2299-2302.

Urbach, F. (ed.) 1969. The Biologic Effects of Ultraviolet Radiation. New York: Pergamon. 704 pp.

APPENDIX A

The Panel's Recommendations

The Committee on Impacts of Stratospheric Change actually made several recommendations. Among them:

▶ Regulation of halocarbons should be selective to produce the greatest immediate reduction in release. In simplest terms, this means that their use in aerosols could be banned by 1978, use in automotive air conditioners and industrial refrigerating units might be restricted several years later, and use in home refrigerators might never be restricted.

▶ In the meantime, all products that contain trichlorofluoromethane and dichlorodifluoromethane which could be released into the atmosphere should be so labeled. This would include aerosols and refill units for auto air conditioners.

▶ The United States should make every appropriate effort to encourage other countries to adopt similar restrictions. This country now accounts for only about half of the halocarbons released into the atmosphere.

▶ Restrictions on halocarbon use should be reviewed every 3 to 5 years, as the amount of knowledge about the climate increases, to determine if such restrictions are appropriate.

▶ A better knowledge of atmospheric chemistry and better measurements of atmospheric species should be obtained. There should also be developed better techniques for modeling both atmospheric and climatic change. Since so little is known in these areas, this should be an adequately financed long-term program.

▶ Better information should be obtained about the effects of ultraviolet radiation on humans, and particularly about its effects on plants and animals.

▶ Research should be undertaken to identify population groups with a drastically higher than normal susceptibility to malignant melanoma.

▶ More information should be obtained about preventive medicine procedures needed to protect humans against ultraviolet-induced skin cancers.

—T.H.M.

APPENDIX B

(To be made one (1) (n copies)

HOUSE OF REPRESENTATIVES
EIGHTH LEGISLATURE, 19 76
STATE OF HAWAII

H.R. NO. 528 H.D. 1

HOUSE RESOLUTION

EXPRESSING CONCERN ABOUT THE POSSIBLE ADVERSE IMPACT OF THE USE OF FLUOROCARBON COMPOUNDS ON THE ENVIRONMENT AND THE WELFARE OF THE PEOPLE OF HAWAII.

WHEREAS, the 1974 Rowland-Molina fluorocarbon/ozone depletion hypothesis indicates that fluorocarbon compounds, when discharged in the atmosphere, impairs the earth's ozone layer; and

WHEREAS, the ozone layer provides protective screening of ultraviolet radiation; and

WHEREAS, significant increases in human exposure to ultraviolet radiation may endanger public health; and

WHEREAS, fluorocarbons are believed to have long atmospheric lifetimes; and

WHEREAS, fluorocarbons have been produced at a rate of about two billion pounds per year; and

WHEREAS, there is considerable debate about the validity of this ozone depletion theory; now, therefore,

BE IT RESOLVED by the House of Representatives of the Eighth Legislature, Regular Session of 1976, that this body express great concern about the possible adverse impact of the use of fluorocarbons on the welfare of our community; and

BE IT FURTHER RESOLVED that this body strongly encourage the United States Congress to direct federal agencies to cooperatively research this problem; and

BE IT FURTHER RESOLVED that this body request the Environmental Center of the University of Hawaii to annually report on new research findings on this ozone depletion theory and to make recommendations on appropriate State legislative action; and

BE IT FURTHER RESOLVED that certified copies of this resolution be transmitted to the Hawaii Congressional Delegation, and the Environmental Center of the University of Hawaii.

EP 862-583